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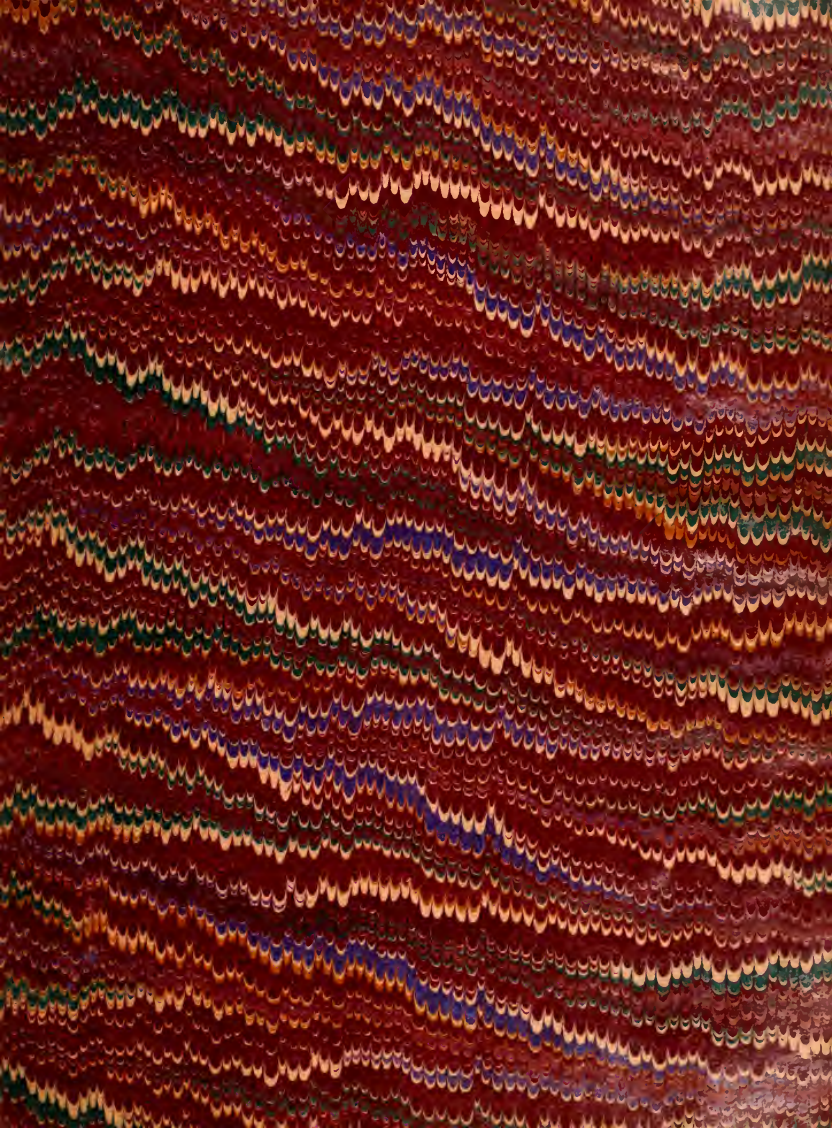
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Johns Hopkins University





- I. An Investigation of the Fatty Oil Contained in
the Seeds of Lindera Benzoin.
- II. Lauric Acid and Some of its Derivatives.

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DISSERTATION

Submitted to the
Board of University Studies
of the
Johns Hopkins University ,
for the
Degree of Doctor of Philosophy,
by

Charles Edward Caspari.

1900.

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CONTENTS.

Page

Acknowledgment	
Introduction	1

Part I.

Examination of the oil contained in the berries of the <u>Lindera Benzoin</u> .	4
Method of extracting the oil	5
Properties of the oil	6
Saponification equivalent of the fat	6
Determination of the volatile and soluble acids in the fat (Reichert's Method)	7
Analysis of the fat	9

Part II.

Lauric acid and some of its derivatives	24
Historical	24
Lauric acid	25
Chloride of lauric acid	27
Amide of lauric acid	28
Anilide of lauric acid	29
Toluid of lauric acid	30
Metallic salts of lauric acid	31
Barium laurate	31
Strontium laurate	32
Calcium laurate	33
Magnesium acid laurate	34

Zinc laurate	35
Copper laurate	36
Lead laurate	36
Manganese laurate	37
Cobalt laurate	38
Biographical sketch	39

ACKNOWLEDGMENT.

The investigation here submitted was undertaken at the suggestion of Professor Ira Remsen to whom I would express the deepest gratitude for the constant interest he has taken in the work and for the zeal which he has inspired both in the lecture-room and in the laboratory. I would also thank Professors Morse and Clark and Doctors H. C. Jones and Mathews for instruction received at their hands.

INTRODUCTION

Stillman and O'Neill⁽¹⁾ undertook an investigation of the fatty oil contained in the fruit of the California bay tree, Umbellularia Californica or Laurus Californica and isolated a new acid, $C_{22}H_{42}O_2$, which they called umbellulic acid. This acid is one of the few exceptions to the general rule that, of the higher members of the fatty acid series, only those occur in nature which contain an even number of carbon atoms. This new acid differs quite markedly from the isomeric undecylic acid, $C_{21}H_{42}O_2$, obtained by Krafft. However, very little is known about umbellulic acid, as no work has been done on it since the publication of the article referred to above.

It was thought possible that, since the Lindera Benzoin belongs to the same family as the California bay tree, it might also contain umbellulic acid or some acid closely related to it, and it was with this possibility in mind that the present investigation was undertaken.

While it has not been possible to isolate umbellulic acid or indeed any acid containing an uneven number of carbon atoms, nevertheless some very interesting results have been obtained.

(1) Amer. Chem. Jour. IV, 206.

Lindera Benzoin, also known as Benzoin odoriferum and Laurus Benzoin and commonly called spicewood, spicebush or feverbush, is a bush growing to the height of twenty feet, frequently much lower, and is indigenous all over the United States. It is found chiefly in damp regions along water courses, and is quite generally used in the southern states by the country people as a remedy against fever and measles. It has a strong odor of spices and contains an ethereal oil in all of its parts. ⁽¹⁾

The oil of its bark and twigs has the odor of wintergreen, boils between 170° and 300° , has the specific gravity 0.923 and contains 9 - 10 per cent of methyl salicylate. The oil from the berries contains about 4 per cent of an oil having a camphoraceous odor, the specific gravity 0.850 - 0.855 and which boils from 160° - 270° . The leaves contain about 0.3 per cent of an oil having the odor of lavender and the specific gravity 0.888.

In this investigation only the oil from the berries has been dealt with. In the neighborhood of Baltimore, where the material was collected, the berries ripen in the middle or latter part of September, and must be gathered very soon after they ripen, otherwise they will fall to the ground and be lost in the undergrowth.

(1) Report of Schimmel & Co., Oct. 1885, 27 and Oct. 1890, 49

When ripe the berries have a bright red color, are oval in shape and are about a half inch long. A half bushel of these were collected in Howard County, Maryland, and were steeped in water for several days until the outer flesh or pulp began to soften and decay. It was then comparatively easy to obtain the inner kernel, entirely free from the softer pulp. The kernels were allowed to dry completely in the air. The half bushel of berries yielded about 2500 grams of kernels.

The investigation is divided into two parts; first, the examination of the oil from the berries, and second, a thorough investigation of lauric acid, which was found in the oil as a glyceride, and of some of its derivatives.

Part J

Examination of the Oil contained in the
Berries of the Lindera Benzoin.

A few grams of the kernels were thoroughly macerated, mixed with ether and extracted for several hours in a Soxhlet extractor. The ether was evaporated from the solution, the residue mixed with water and subjected to distillation with steam. An extremely small amount of oil distilled over, which contained all the odorous material of the oil, since the residue after distillation was entirely odorless. However, the amount of volatile oil was so very small that it was impossible to obtain enough of it from the amount of material at hand for investigation and so the work was confined to that portion of the oil which is not volatile with water vapor. It is hoped at some later day to complete the examination of the volatile oil.

A quantitative determination of the oil contained in the seeds gave the following result: 3.2809 grams seeds yielded 1.9065 grams oil which is equivalent to 58.10 per cent. This result is a trifle too high because it was impossible to prevent a small amount of the finely divided pulp from filtering through the paper thimble of the Soxhlet extractor, and this pulp was then weighed

with the oil, but the error is only a very small one.

Method of Extracting the Oil.

Some difficulty was experienced in obtaining a satisfactory method for extracting the oil from the seeds.

It was first attempted to extract all the material with ether in a Soxhlet extractor, but this method was unsatisfactory from two causes. In the first place some of the pulp was always present in the oil, and it was practically impossible to filter it off, and in the second place the extractors at hand were so small that it would have entailed a great loss of time to have extracted all the seeds in that way. It was then attempted to moisten the macerated pulp with ether, and express the mass in a hand press which was available. This method gave the oil free from pulp, but the yield was only about 60 per cent of what it should have been. Finally, Professor Remsen wrote to Messrs. Fritzsche Brothers in Garfield, New Jersey, asking them whether they would extract the seeds for us. They very kindly consented to do so, and I take this opportunity of thanking them for their kindness. They expressed the seeds, and then extracted the expressed mass with petroleum ether boiling from 40° - 50°. After evaporating the petroleum ether the extracted and expressed oils were distilled with steam for several hours, but the amount of volatile oil

was so small that they did not consider it worth the trouble of isolating it. From 2130 grams of the seeds were obtained

735 grams = 34.5 per cent of expressed oil

237 grams = 11.1 per cent " extracted "

Total 972 grams = 45.6 per cent.

Properties of the Oil.

The product obtained from Messrs. Fritzsche Brothers was a solid fat. It was yellow in color, and quite crystalline throughout its structure. It melted at 26° . The fat is very soluble in ethyl alcohol, benzene, gasoline and acetone, but is more difficultly soluble in anhydrous methyl alcohol. Its solution in ethyl alcohol reacts neutral towards litmus.

Saponification Equivalent of Fat.

1.9311 grams of fat were saponified with 77.31 c.c. of a standard alcoholic solution of caustic potash. After saponification 6.32 c.c. of standard acid were required to neutralize the excess of alkali.

6.32 c.c. acid \equiv 6.57 c.c. alkali.

$77.31 - 6.57 = 69.74$ c.c. alkali required for saponification.

1 c.c. alkali contained 0.007875 gram caustic potash.

A. 1.9311 grams fat require for saponification 0.5492

gram caustic potash and 1 gram fat requires 284.4 milligrams caustic potash for saponification.

Determination of the Volatile and Soluble Acids in the Fat (Reichert's Method)

The saponified material obtained in the above determination was used for this determination. The alcohol was evaporated and the potassium salts were dissolved in water. The fatty acids were set free by dilute sulphuric acid. After diluting with water, the mixture was distilled so that 110 c.c. of distillate were obtained in a half hour. This distillate was then filtered and titrated with $\frac{N}{10}$ caustic potash using phenolphthalein as an indicator. The amount of alkali required for neutralization was 0.998 c.c. The weight of fat used was 1.9311 grams. Therefore 2.5 grams of fat would require 1.29 c.c. $\frac{N}{10}$ caustic potash to neutralize the volatile and soluble acids contained in it. Hence the Reichert number is 1.29. Another determination gave the value 1.34.

These results show that the percentage of volatile and soluble acids obtained from the fat is very small, and they doubtless consist of small amounts of capric acid, $C_{10}H_{20}O_2$, which was later found in the fat as the glyceride, and which is volatile with steam and slightly soluble in water.

-should I say whether anyone I see has been treated with
methamphetamine or has been given drugs

QUESTIONER: WHAT ABOUT THE CHARGES?

ANSWER: I REMEMBER ALL OF IT.

QUESTIONER: I BELIEVE I BELONGED WITH YOU AT

THESE TWO INSTITUTIONS WITH YOU AND YOUR MOTHER
WHEN YOU WERE THERE, WERE YOU NOT THERE FOR

THE SAME REASON AS YOU ARE NOW THERE, THAT YOU WERE
TREATED WITH METHAMPHETAMINE AND YOU WERE

IN THE HOSPITAL FOR A LONG TIME, IS THAT RIGHT?

ANSWER: YES, THAT IS RIGHT. I WAS THERE FOR ABOUT
THREE YEARS BEING TREATED BY THE MEDICAL STAFF

IN ORDER TO MAKE ME BEHAVIOR AS AN INSTITUTIONAL
PATIENT AND I WAS THERE BEHAVIORING FOR THE

REASON THAT I WAS THERE. WHEN THE COURT MADE THE
DETERMINATION THAT I HAD AN IQ OF 70, MY

WIFE, MY BROTHER, MY SISTER, ALL OF THEM, ALL
OF THEM, ALL OF THEM, ALL OF THEM, ALL OF THEM, ALL

OF THEM, ALL OF THEM.

QUESTIONER: WERE YOU EVER TREATED WITH

DRUGS, WERE YOU EVER TREATED WITH DRUGS, WERE YOU
EVER TREATED WITH DRUGS, WERE YOU EVER TREATED

WITH DRUGS, WERE YOU EVER TREATED WITH DRUGS, WERE
YOU EVER TREATED WITH DRUGS, WERE YOU EVER

TREATED WITH DRUGS?

While the distillation in determining the Reichert number was in progress, it was noticed that a small amount of some material came over, which was insoluble in water and solid at ordinary temperatures. Some of this material was collected and dissolved in alcohol and this solution reddened blue litmus paper. The solution was heated to boiling and to it was added a hot solution of lead acetate in alcohol. Very soon fine delicate needles, clustering together in rosettes appeared, and when the solution had cooled these were filtered off, washed well with water and with alcohol and dried over calcium chloride. Analysis of the salt yielded the following results:

I. 0.1460 gram of salt gave 0.0757 gram PbSO₄.

II. 0.3128 gram of salt gave 0.1581 gram PbSO₄.

Calculated for

Pb (C₁₂H₂₃O₂)₂
Pb 34.17

Found.

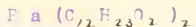
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I	II
35.34	34.52

The barium salt of the same acid was made by treating a boiling alcoholic solution of the acid with a boiling alcoholic solution of barium acetate. The salt was washed, dried over calcium chloride and analyzed with the following results:

I. 0.2629 gram of salt gave 0.1157 gram BaSO₄.

II. 0.2203 gram of salt gave 0.0971 gram BaSO₄.

Calculated for



Ba 25.64

Found

I II.

25.87 25.92

From the above analytical results it would seem that the acid was lauric acid, which is difficultly volatile with water vapor and which is insoluble. However, through subsequent work this conclusion was shown to be wrong, and the explanation of the above results will be given further on.

Analysis of the Fat.

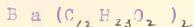
To make sure that the barium salt mentioned above was a salt of lauric acid alone, it was subjected to fractional crystallization from water, in which it is quite insoluble.

Two or three grams of the barium salt were boiled with two liters of water. A portion of it dissolved and was filtered boiling hot. Immediately crystals began to separate out, and after about fifteen minutes these were filtered off, dried and analyzed.

0.1836 gram of salt gave 0.0895 gram BaSO₄.

Calculated for

Found.



Ba 25.65

25.75

When the above filtrate had cooled to the tempera-

ture of the room, more crystals had separated out. These were filtered off, dried over calcium chloride and analyzed.

0.1340 gram of salt gave 0.0611 gram B a S O₄.

	Calculated for	Calculated for	Calculated for	Found
	B a(C ₁₂ H ₁₃ O ₂) ₂	B a(C ₁₁ H ₁₁ O ₂) ₂	B a(C ₁₀ H ₉ O ₂) ₂	
B a	25.65	27.06	28.64	26.84

The filtrate from the second crop of crystals was concentrated considerably by evaporation, and when the solution had cooled, crystals again separated out. After drying over calcium chloride they were analyzed.

0.2582 gram of salt gave 0.1237 gram B a S O₄.

Calculated for	Found
B a(C ₁₀ H ₉ O ₂) ₂	
B a 28.64	28.27

Next, the crystals which were found to contain 26.84 per cent of barium were dissolved in boiling water, and the solution was allowed to cool to the temperature of the room. The crystals which had separated out were dried and analyzed.

0.2306 gram of salt gave 0.1017 gram B a S O₄.

Calculated for	Found
Ba (C ₁₂ H ₂₃ O ₂) ₂	
Ba 25.65	25.95

The filtrate from these crystals was evaporated down, and upon cooling a second crop of crystals separated out. These were likewise dried and analyzed.

0.1994 gram of salt gave 0.0959 gram Ba SO₄.

Calculated for	Found
Ba (C ₁₀ H ₁₉ O ₂) ₂	
Ba 28.64	28.32

Finally, that portion of the original barium salt, which was insoluble in boiling water, was boiled with more water and went completely into solution. It had not dissolved before because there had not been enough water present. Almost as soon as boiling ceased, crystals began to separate out quite rapidly and these were filtered off while the solution was still quite hot. After drying over calcium chloride they gave the following result upon analysis.

0.2589 gram of salt gave 0.1114 gram Ba SO₄.

Calculated for	Found
Ba (C ₁₂ H ₂₃ O ₂) ₂	
Ba 25.65	25.33

The filtrate from these crystals, when cooled down to the temperature of the room, did not deposit enough crystals to make an analysis, and when concentrated considerably by evaporation and cooled, not enough material separated out for analysis.

This fractional crystallization of the barium salt offers very strong evidence in favor of the fact that the material which is volatile with steam and insoluble in water, obtained when the mixed acids derived from the fat are distilled with steam, consists not of lauric acid alone, but of lauric and capric acids. Of the first three fractions obtained, the first one approximates very closely to barium laurate, the third one to barium caprate, while the second one gives an analysis which agrees very well with that demanded by barium undecylate, $\text{Ba}(\text{C}_{11}\text{H}_{21}\text{O}_2)_2$, but the second one when redissolved and subjected to fractional crystallization can be resolved into two salts whose barium content agrees very well with that of barium laurate and barium caprate. Finally, that portion of the original barium salt which remained undissolved, when it was first boiled with water, dissolved completely when more water was added, and upon crystallization yielded practically only barium laurate. This can be explained only if barium laurate and barium caprate were originally present. The first time the barium salt was boiled with

water, a large part of the barium laurate and all of the barium caprate went into solution, because barium caprate is much more soluble in water than barium laurate, and the residue which dissolved completely when boiled again with water consisted entirely of barium laurate, and did not dissolve at first on account of its great insolubility in water.

It now seems clear why the lead and barium salts described on pages 8 and 9 gave analytical results agreeing so well with those of barium laurate and lead laurate. Evidently in each case lead acetate and barium acetate had been added in quantities insufficient to precipitate the acids completely. Only the lead and barium laurates crystallized out with perhaps a very little of the caprates because the caprates are so much more soluble than the laurates in alcohol, as well as in water.

The fractional crystallization of the barium salt of the mixed acids, and the subsequent liberation of the free acids from their separated salts does not offer a very expedient method for the separation of the pure acids, because such an enormous amount of water is required to dissolve the original barium salts. Hence it was thought best to saponify the fat, liberate the free

acids and subject them to fractional distillation under diminished pressure. In this way it is possible to separate the individual acids quite thoroughly.

Accordingly, about 250 grams of the fat obtained from Fritzsche Brothers was saponified with an alcoholic solution of potassium hydroxide (66 grams to the liter). After the alcohol was distilled from the saponified material, there was left a dark brown, pasty mass which consisted of the potassium salts of the fatty acids together with any glycerol which might have been present in the fat in the form of glycerides. This dark residue was dissolved completely in cold water, and from this solution were precipitated the free acids by means of dilute sulphuric acid. They are solid at ordinary temperatures, and float on the aqueous solution. The entire mass was heated on the water-bath until the acids had melted and had collected completely at the surface. Upon cooling, the acids formed a solid cake, which could be easily lifted off from the aqueous solution. This aqueous solution was filtered, neutralized with potassium hydroxide and evaporated almost to dryness. The residue was extracted five times with absolute alcohol, and this alcoholic solution was afterwards examined for glycerol. The fatty acids were heated on the water-bath for ten to twelve hours in order to dry them as much as

possible before distilling them

The apparatus used for distillation under diminished pressure was that recommended by Anschütz. It consisted of two distilling bulbs, the side tube of one fitting into the neck of the other, which was the receiver. The side tube of the receiver was connected with a manometer, which in turn was connected with an ordinary filter pump. Only rubber stoppers and very thick walled rubber tubing were used in making connections. A capillary tube, through which a small current of air was constantly kept passing, dipped under the surface of the boiling liquid and thus rendered the ebullition more regular, preventing any liquid from passing over into the receiver (which was not first vaporized). The distilling bulb was never more than one-third filled, and was placed in an iron dish, the bottom of which was covered with fine asbestos, so that the bulb could not come in contact with the metal, and then heat was applied to the iron dish. The temperature of the air-bath was never allowed to rise more than 40° higher than the temperature of the vapor in the distilling bulb. No condenser tube was necessary, since the acids boiled so high that the side tube of the distilling bulb was sufficiently long to condense all the vapors.

Under 11 to 15 mm. pressure, the acids which had

been dried on the water-bath, began to boil at 150° , and from the first distillation two fractions were collected, from 150° to 170° and from 170° - 185° . The portion boiling above 185° was reserved for examination later on. These two fractions were then redistilled and three fractions were collected under 12 to 14 m.m. pressure, from 154° - 157° , from 157° - 166° and from 166° - 187° . In the last fraction most of the distillate came over at about 168° . During the distillation the temperature of the air-bath varied from 190° - 220° . The first and third fractions contained approximately equal volumes, while the volume of the intermediate fraction was much smaller than that of the first or third. These three fractions were colorless when liquid and white when solid, with a decidedly crystalline structure. The barium salts of the acids in the first and third fractions were made by bringing together a boiling alcoholic solution of the acid with a concentrated boiling solution of barium acetate in about 50 per cent alcohol. After being washed with alcohol and with water, and dried in the air these salts were analyzed for barium with the following results.

Fraction boiling from 154° - 157° under 12 to 14 m.m. pressure.

I. 0.2144 gram of salt gave 0.1025 gram of BaSO_4 .

II 0.2321 gram of salt gave 0.1107 gram of BaSO₄.

Calculated for		Found	
Ba (C ₁₀ H ₁₉ O ₂) ₂		I.	II.
Ba	28.64	28.15	28.08

Fraction boiling from 166° - 187° under 12 to 14 m.m. pressure.

I. 0.2935 gram of salt gave 0.1281 gram of BaSO₄.

II. 0.2918 gram of salt gave 0.1274 gram of BaSO₄.

Calculated for		Found.	
Ba (C ₁₂ H ₂₃ O ₂) ₂		I.	II.
Ba	25.65	25.69	25.77

From these results the conclusion may be drawn that the fraction boiling from 154° - 157° consisted mainly of capric acid with perhaps a very little lauric acid, and that the fraction boiling from 166° - 187° consisted of quite pure lauric acid.

In order to obtain a purer capric acid the fraction boiling from 154° - 157° was redistilled, together with the intermediate fraction mentioned above, which under the same pressure boiled from 157° - 166°. From this distillation three fractions were obtained, the first boiling from 156° - 157° under 15 m.m. pressure, the second boiling from 157° - 154° under 10 - 11 m.m. pressure and the third from 157° - 169° under 13 m.m.

pressure. The first fraction had by far the largest volume, while the second and third fractions each had a volume which was much smaller than that of the fraction boiling from 157° - 166° under 10 to 12 m.m. pressure. These facts show that this last mentioned fraction was composed of a lower and a higher boiling portion. The analyses below show that it consisted of a mixture of capric and lauric acids.

The barium salts of the three new fractions were made exactly as those described above, and upon analysis gave the following results for barium.

Fraction boiling from 156° - 157° under 15 m.m. pressure.

- I. 0.2007 gram of salt gave 0.0965 gram of BaSO₄.
 II. 0.2315 gram of salt gave 0.1115 gram of BaSO₄.

Calculated for		Found.	
		I.	II.
Ba	(C ₁₀ H ₁₉ O ₂) ₂	28.31	28.35

Fraction boiling from 150° - 154° under 10 - 11 m.m. pressure.

- I. 0.2656 gram of salt gave 0.1254 gram of BaSO₄.
 II. 0.2017 gram of salt gave 0.0948 gram of BaSO₄.

Calculated for		Calculated for		Found	
				I.	II.
Ba	(C ₁₀ H ₁₉ O ₂) ₂	Ba	(C ₁₂ H ₂₃ O ₂) ₂	27.76	27.67
Ba	28.64	25.65			

Fraction boiling from 157° - 169° under 13 mm. pressure.

I. 0.2240 gram of salt gave 0.0997 gram of BaO.

II. 0.2573 gram of salt gave 0.1148 gram of BaO.

Calculated for		Calculated for	Found.	
Ba (C ₁₀ H ₁₉ O ₂) ₂		Ba (C ₁₂ H ₂₅ O ₂) ₂	I.	II.
Ba	28.64	25.65	26.20	26.27

Thus, the first fraction consists of practically pure capric acid, the second fraction of capric acid with a little lauric acid and the third fraction of lauric acid with a very much smaller amount of capric acid. From this it appears evident that no acid of the formula C₁₁H₂₂O₂ was present, a conclusion also arrived at from the evidence presented by the fractional crystallization of the barium salts of the mixed acids, when the barium salt containing 26.84 per cent of barium, the percentage of barium in the barium salt of C₁₁H₂₂O₂ being 27.06, was resolved into barium caprate and barium laurate.

There still remain to be considered the residue obtained from the mixed acids which boil above 185° under 11 - 15 m.m. pressure, and the filtrate from the crude acids just after they were set free from their potassium salts, which contained any glycerol that might have been present in the fat as glycerides. The former will be discussed first.

A small portion of the residue boiling above 185° under 11 - 15 m.m. pressure was dissolved in chloroform and treated with bromine water. The color of the bromine disappeared immediately, showing the presence of some unsaturated acid. To test whether this acid was formed during the distillation by decomposition from lauric and capric acids, some of the original fat was treated in solution in chloroform with bromine water and again the color disappeared immediately, showing that the unsaturated compound was present as such in the original fat. The high-boiling residue was distilled under 10 m.m. pressure. Up to 218° very little distillate was obtained, and this was doubtless impure lauric acid, as it solidified almost immediately. From 218° - 225° a very appreciable amount of a clear liquid distilled over, and above 225° the mass carbonized. The distillate which came over between 218° and 225° melted at 13° , the melting point of oleic acid being given as 14° . A hot alcoholic solution of the acid, which did not redden blue litmus paper, another characteristic of oleic acid, was treated with ammonium hydroxide and barium chloride and filtered hot. Upon cooling, a voluminous white crystalline precipitate separated out, which upon analysis gave the following results.

- I. 0.2372 gram of salt gave 0.0786 gram P a % 04
 II. 0.2147 gram of salt gave 0.0710 gram P a % 04.

Calculated for		Found	
Ba (C ₁₈ H ₃₃ O ₂) ₂		I.	II.
Ba	19.63	19.51	19.47

These results point to the conclusion that the acid boiling from 218° - 225° under 10 m.m. pressure is oleic acid. Krafft and Nordlinger⁽¹⁾ give 223° as the boiling point of oleic acid under 10 m.m. pressure. Another piece of evidence also showed that oleic acid is contained in the fat. It is well known that lead oleate is soluble in ether while the lead salts of the saturated acids are not. Accordingly, the potassium salts of the mixed acids from the fat were treated in aqueous solution with a solution of lead acetate. A copious white creamy precipitate was immediately thrown down, and was filtered off and dried as well as possible in the air. It was then extracted with ether several times, and the solution in ether was evaporated down considerably when a yellowish crystalline mass separated out. This mass was recrystallized from ether, and was finally obtained as a white crystalline powder, which melted at about 80° to a yellow liquid. Upon analysis for lead it gave the following results.

(1) Ber d deutsch Chem. Gesell. 22, 819.

- I. 0.2437 gram of salt gave 0.0953 gram P b S O₄.
 II. 0.2156 gram of salt gave 0.0845 gram P b S O₄.

Calculated for		Found.	
		I.	II.
P b (C ₁₈ H ₃₃ O ₂) ₂			
P b	26.88	26.69	26.75

These two pieces of evidence, one from the acids after distillation, the other from the crude acids leave little doubt that oleic acid is contained in the original fat.

It will be remembered that when the fat had been saponified and the acids set free, the aqueous filtrate from the acids was neutralized with potassium hydroxide, evaporated almost to dryness, and that the residue was extracted several times with absolute alcohol. This alcoholic solution was then examined for glycerol. The alcohol was evaporated off and there was left a thick viscous liquid that was quite sweet to the taste, which was heated to 170° in order to drive off all traces of alcohol and water. Portions of this residue were heated in a test tube with about twice their mass of acid potassium sulphate when the disagreeable penetrating vapors of acrolein were evolved proving that the thick liquid above mentioned was glycerol.

Let \mathcal{H} be a Hilbert space and \mathcal{H}^* its dual space. Then

$\mathcal{H}^* \cong \mathcal{H}$ if and only if \mathcal{H} is reflexive.

Hilbert Space		Dual Space	
\mathcal{H}	\mathcal{H}^*	\mathcal{H}	\mathcal{H}
\mathcal{H}^*	\mathcal{H}	\mathcal{H}	\mathcal{H}

Let \mathcal{H} be a Hilbert space and \mathcal{H}^* its dual space. Then

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Let \mathcal{H} be a Hilbert space and \mathcal{H}^* its dual space. Then

$\mathcal{H}^* \cong \mathcal{H}$ if and only if \mathcal{H} is reflexive.

Let \mathcal{H} be a Hilbert space and \mathcal{H}^* its dual space. Then

It is clear from the results here given that the fatty oil or fat of the seeds of the Lindera Benzoin consists of a mixture of the glycerides of capric, lauric and oleic acids. No quantitative determinations of the amount of each acid present were made, but the lauric acid is present in largest proportion.

Part II.

LAURIC ACID AND SOME OF ITS DERIVATIVES.

Historical.

-----:-----

Lauric acid was discovered in 1842 in Liebig's laboratory by Marsson.⁽¹⁾ He obtained it by saponifying the fat contained in laurel berries, and called it laurostearic acid. The acid with which he worked melted at 42° - 43°. Sthamer⁽²⁾ obtained lauric acid from the fat contained in pichurim beans from South America by saponification. His acid melted at 43°. A few years later Gorgey⁽³⁾ during an extensive investigation of coconut oil found that it contained lauric acid. Capric and caprylic acids were also present, and he separated the three acids by a fractional crystallization of their barium salts. He described lauric acid very much as Marsson and Sthamer had done and said it melted at 42°-43°. Heintz⁽⁴⁾ obtained lauric acid which melted at 43.6° from whale fat. In 1867, Oudemans⁽⁵⁾ found lauric acid as a constituent of Pangkallak fat obtained from the Cylicodaphne sebifera of Java. Oudemans⁽⁶⁾ in 1863

(1) Ann. 41, 329. (2) Ann. 53, 390. (3) Ann. 66, 290.

(4) Ann. 92, 294. (5) Zeit. f. Chem. 1867, 256.

(6) Jour. f. prakt. Chem. 39, 206.

(1) H_2O

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prepared and described several of the salts of lauric acid. He did not state the source or the melting point of his acid, and since many of his results differ considerably from those obtained with the lauric acid from the seeds of Lindera Benzoin, it is questionable whether Oudemans was dealing with perfectly pure lauric acid. As most of the work on lauric acid was done more than forty years ago, it seemed desirable that some of the work should be repeated with the aid of modern improvements in chemical methods.

LAURIC ACID.



The method of obtaining lauric acid from the seeds of Lindera Benzoin has already been described. The acid melts at 42° and boils at 166° under 10 - 11 m.m. pressure. It is very soluble in alcohol from which it can be crystallized in warty crystals, which have a satin lustre. It is practically insoluble in water. In alcoholic solution it turns blue litmus paper red. Upon analysis the acid gave the following results.

- I. 0.2432 gram of acid gave 0.6398 gram CO_2 and
0.2662 gram H_2O .
- II. 0.2314 gram of acid gave 0.6083 gram CO_2 and
0.2557 gram H_2O .

Calculated for



C 71.91

H 12.10

Found

	Found	
	I	II.
C	71.75	71.69
H	12.17	12.27

In order to be sure that this acid is identical with that obtained by Krafft⁽¹⁾ from laurel oil, from whose results those here given differ somewhat, a half kilogram of laurel oil was purchased from Dodge and Olcott in New York, which yielded about ten per cent of lauric acid by saponification and distillation under diminished pressure. This acid melted at 42° and boiled at 166° under 11 m.m. pressure and was in all respects identical with that obtained from the seeds of the Lindera Benzoin. Krafft said that his acid melted at 43.5° .

Of the sources of lauric acid thus far discovered the seeds of the Lindera Benzoin yield it most abundantly and with comparatively little difficulty.

(1) Ber. d. chem. Ges. 12, 1664

The Chloride of Lauric Acid.



The chloride⁽¹⁾ of the acid was made by treating the melted acid with a little more than the calculated amount of phosphorus trichloride and heating the mixture on the water-bath for fifteen or twenty minutes, until the action was complete. In this reaction only the chloride of the acid and phosphorous acid are formed. The latter sinks to the bottom of the dish as a rather viscous liquid so that the chloride can be poured from it very easily. In order to purify this crude chloride, it was subjected to distillation under diminished pressure and after one distillation it yielded the following analytical results.

I. 0.3772 gram of chloride gave 0.2447 gram A g C l.

II. 0.2264 gram of chloride gave 0.1474 gram A g C l.

Calculated for



C l 16.21

Found

I II

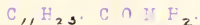
16.04 16.09

The chloride is decomposed slowly by the moisture in the air, and must hence be well protected from the air. It is also decomposed very quickly by alcohol.

(1) Ber. d. chem. Gesell. 31, 2344.

According to Kraft⁽¹⁾ it boils at 142.5° under 15 m.m. pressure, and melts at -17° . That which gave the above results boiled at 145° under 18 m.m. pressure, and remained liquid when cooled down to -17° .

The Amide of Lauric Acid.



The amide of lauric acid was made according to the method for the general preparation of acid amides recommended by Aschan.⁽²⁾ It was his method that was used in making the acid chloride. The chloride was added drop by drop to an excess of a well cooled, concentrated solution of ammonia, which was constantly stirred. The amide was precipitated out immediately, as it is insoluble in water. It was crystallized several times from 50 per cent alcohol until its melting point remained constant after three crystallizations. The amide crystallizes in very fine feathery white needles, which when dry have a very fluffy appearance with a satin lustre. It melts sharply between 98° and 99° . Upon analysis it gave the following results.

0.1689 gram of amide gave 0.4492 gram of CO_2 and

0.1938 gram of H_2O

(1) Ber. d. Chem. Gesell. 17, 1378.

(2) Ber. d. Chem. Gesell. 31, 2344.

Calculated for	Found
$C_{11}H_{23} \cdot CO \cdot NH_2$	
C 72.26	72.53
H 12.67	12.73

0.3202 gram of amide gave 0.0228 gram of N.

Calculated for	Found
$C_{11}H_{23} \cdot CO \cdot NH_2$	
N 7.02	7.13

The nitrogen was determined as ammonia by the Kjeldahl method.

The amide of lauric acid has been made only once before, and then by Krafft.⁽¹⁾ He does not give any analyses of his product nor does he say how he purified it. His amide melted at 102°.

The Anilid of Lauric Acid.



The anilid of lauric acid has never been made before. It was made by adding lauryl chloride drop by drop to an emulsion in water of twice the calculated amount of aniline required. Reaction took place immediately. The excess of aniline was removed as hydrochloride with hydrochloric acid. The product of the reaction was crystallized several times from 50 per cent al-

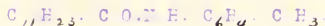
(1) Ber. d. chem. Gesell. 15, 1729.

cohol, and finally it melted constantly before and after two crystallizations at 76.5°. The anilid crystallizes quite well in long, feathery, fluffy white needles resembling finely shredded asbestos. It was analyzed for nitrogen by the Kjeldahl method with the following result.

0.2548 gram of anilid gave 0.0133 gram N.

Calculated for	Found
$C_{11}H_{23} \cdot C_6H_5 \cdot N \cdot H \cdot C_6H_5$	
N 5.10	5.20

The Toluid of Lauric Acid.



The toluid of lauric acid was made similarly to the anilid. Lauryl chloride was dropped into an aqueous emulsion of orthotoluidine and the resulting toluid was crystallized several times from 50 per cent alcohol. It forms very fine light white needles, which melt at 81.5°. A determination of nitrogen yielded the following result by the Kjeldahl method.

0.2496 gram of toluid gave 0.0119 gram of N.

Calculated for	Found
$C_{11}H_{23} \cdot C_6H_4 \cdot N \cdot H \cdot C_6H_4 \cdot C_6H_3$	
N 4.84	4.79

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The amide, anilid and toluid of lauric acid resemble each other very closely in appearance and in their solubility. They are all insoluble in water and easily soluble in 95 per cent alcohol. The best menstruum from which to crystallize them is 50 per cent alcohol.

Metallic Salts of Lauric Acid.

Barium Laurate.



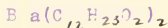
Barium laurate was made by bringing together a boiling solution of lauric acid in 95 per cent alcohol and a boiling solution of barium acetate in 50 per cent alcohol. Almost immediately after mixing the two solutions the crystals of barium laurate separated out. They consist of very fine white needles which cluster together forming rosettes, which when dry have a lustre resembling that of mother of pearl or of fish scales.

Barium laurate is very difficultly soluble in water and in alcohol and does not melt when heated to 160° . It yielded the following analytical results for barium.

I. 0.4751 gram of salt gave 0.2061 gram of BaSO_4 .

II 0.4351 gram of salt gave 0.1897 gram of BaSO_4 .

Calculated for



Ba 25.64

Found

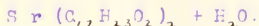
I II

25.54

25.66

Oudemans⁽¹⁾ describes barium laurate as amorphous, while as a matter of fact it is quite crystalline.

Strontium Laurate.



Strontium laurate was made by mixing a boiling solution of lauric acid in 95 per cent alcohol with a boiling solution of strontium acetate in 50 per cent alcohol. Before the solution had cooled crystals of strontium laurate separated out. These consisted of fine white needles which clustered together, but did not have the pearly lustre of barium laurate. Strontium laurate is as insoluble in water as barium laurate and nearly as insoluble in alcohol. It decomposes without melting at about 240° and contains one molecule of water of crystallization.

I. 0.2177 gram of salt gave 0.0076 gram H_2O .

II. 0.2236 gram of salt gave 0.0077 gram H_2O .

Calculated for	Found	
	I	II
$\text{Sr} (\text{C}_{12}\text{H}_{23}\text{O}_2)_2 + \text{H}_2\text{O}$		
H_2O 3.57	3.51	3.48

I. 0.2101 gram of anhydrous salt gave 0.0790 gram SrSO_4 .

II. 0.2159 gram of anhydrous salt gave 0.0811 gram SrSO_4 .

(1) Jour. f. prakt. Chem. 89, 206.

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Residence [Address] [City] [State] [Zip]

[Name] [Address]

[City] [State] [Zip]

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Calculated for	Found	
	I	II
Sr $(C_{12}H_{23}O_2)_2$		
Sr 18.02	17.96	17.93

Calcium Laurate.



Calcium laurate was made similarly to the barium and strontium salts. It is much more soluble in alcohol than either of these salts and crystallizes in very short delicate white needles, which cannot be distinctly seen without the aid of a pocket lens. The crystals contain one molecule of water of crystallization and melt at $182^\circ - 183^\circ$.

I. 0.2145 gram of salt gave 0.0075 gram of H_2O .

II. 0.2027 gram of salt gave 0.0070 gram of H_2O .

Calculated for	Found	
	I	II
Ca $(C_{12}H_{23}O_2)_2 + H_2O$		
H_2O 3.94	3.49	3.45

This salt is efflorescent, and this fact accounts for the somewhat low results obtained in the determination of water of crystallization.

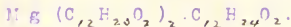
I. 0.2070 gram of anhydrous salt gave 0.0657 gram of $CaSO_4$.

II. 0.1957 gram of anhydrous salt gave 0.0613 gram of



Calculated for		Found	
		I	II
Ca	$(C_{12}H_{23}O_2)_2$		
Ca	9.12	9.33	9.21

Magnesium Acid Laurate.



This salt was obtained by treating a hot alcoholic solution of lauric acid with a hot neutral alcoholic solution of magnesium acetate. It was expected that the normal magnesium laurate would be formed, but in two instances the acid salt was obtained, and it was impossible to obtain the normal salt. This case of magnesium forming an acid salt seems to be an isolated one. The salt is the most soluble salt of lauric acid, with the exception of potassium and sodium laurates. It crystallizes most readily from 50 per cent alcohol in very fine white needles which melt at 74°- 75°. Analyses for magnesium gave the following results.

- I. 0.2017 gram of salt gave 0.0377 gram of $MgSO_4$.
 II. 0.2591 gram of salt gave 0.0486 gram of $MgSO_4$.

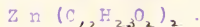
Calculated for.		Found.	
		I	II
Mg	$(C_{12}H_{23}O_2)_2 \cdot C_{12}H_{24}O_2$		
Mg	3.91	3.79	3.79

Oudemans ⁽¹⁾ described the normal magnesium laurate, $Mg(C_{12}H_{23}O_2)_2$, and said it contained three molecules of

(1) loc. cit.

water of crystallization. Strange to say his salt melted at 75° , the melting point of the acid salt described above. Oudemans did not state how he prepared his magnesium laurate.

Zinc Laurate.

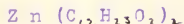


Zinc laurate was made as the previous salts were, by bringing together a hot alcoholic solution of lauric acid and a hot alcoholic solution of zinc acetate. The salt is moderately soluble in alcohol and crystallizes in delicate white needles which cluster together similarly to the barium salt and form rosettes. It also has the pearly or satin lustre which the barium salt has.

I. 0.2067 gram of salt gave 0.0365 gram of Zn O.

II. 0.2209 gram of salt gave 0.0388 gram of Zn O.

Calculated for



Zn 14.09

Found

I

II

14.18 14.07

This salt dried in the air and contained no water of crystallization. Oudemans⁽¹⁾ described a zinc laurate to which he gave the formula $\text{Zn} (\text{C}_{12}\text{H}_{23}\text{O}_2)_2 + \text{H}_2\text{O}$ and which melted at 80° . The salt described above melts at 127° .

(1) Loc. cit.

Copper Laurate.

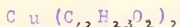


Copper laurate was made just as the previously described salts were, and separates out from solution as a light bluish green microscopically crystalline powder. It is very difficultly soluble in alcohol and insoluble in water. When heated, it gradually turns darker and finally assumes a dark green color. It does not melt when heated up to 220° .

I. 0.2048 gram of salt gave 0.0349 gram of Cu O.

II. 0.2110 gram of salt gave 0.0359 gram of Cu O.

Calculated for



Cu 13.76

Found

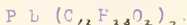
I

II

13.62 13.59

Oudemans⁽¹⁾ described a copper laurate, $\text{Cu} (\text{C}_{12}\text{H}_{23}\text{O}_2)_2$, which he said melted at 90° , while the above described salt does not melt when heated to 220° .

Lead Laurate.



Lead laurate was made similarly to the other salts. It is insoluble in water, but may be crystallized from alcohol. It crystallizes in delicate white needles which

(1) Loc. cit.

Page 10

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Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
10	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

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have a pearly lustre and which melt at 101° . Oudemans⁽¹⁾ described his lead laurate as being amorphous, while the salt here described forms definite crystals with comparatively little difficulty.

I. 0.2757 gram of salt gave 0.1382 gram of $PbSO_4$.

II. 0.2580 gram of salt gave 0.1294 gram of $PbSO_4$.

Calculated for

Found

$Pb(C_{12}H_{23}O_2)_2$

I

II

Pb 34.18

34.22

34.23

Manganese Laurate.

$Mn(C_{12}H_{23}O_2)_2$

Manganese laurate was prepared as the other salts were. It is insoluble in water, but is soluble in alcohol. It separates out from its solution as a very pale pink, microscopically crystalline powder so that the crystal form could not be determined. It melts at 76° and contains no water of crystallization. Oudemans⁽²⁾ described a manganese laurate melting at 75° and containing x molecules of water of crystallization.

I. 0.2202 gram of salt gave 0.0724 gram of $MnSO_4$.

II. 0.2327 gram of salt gave 0.0761 gram of $MnSO_4$.

Calculated for

Found

$Mn(C_{12}H_{23}O_2)_2$

I

II

Mn 12.13

11.97

11.91

(1) *Ann. Chem. Phys.* (3) 1867, 4, 100.

(2) *Ann. Chem. Phys.* (3) 1867, 4, 100.

Cobalt Laurate.

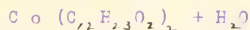


Cobalt laurate was made as the other salts were and is quite soluble in alcohol but insoluble in water. It forms delicate, pale red needles which melt at 52° , and then assume a dark violet color. The cobalt laurate described by Gudemans⁽¹⁾ contained one molecule of water of crystallization but melted at 75° .

I. 0.2211 gram of salt gave 0.0078 gram of H_2O .

II. 0.2070 gram of salt gave 0.0074 gram of H_2O .

Calculated for



H_2O 3.79

Found

I

II

3.53

3.57

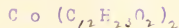
I. 0.2133 gram of anhydrous salt gave 0.0716 gram of



II. 0.1996 gram of anhydrous salt gave 0.0660 gram of



Calculated for



Co 12.89

Found

I

II

12.77

12.71

(1) loc. cit.

BIOGRAPHICAL.

The author of this dissertation was born in Baltimore, Maryland, on the 9th of April 1875. His early education was obtained in the public schools of Baltimore, and he graduated from the Baltimore City College in 1893. In the fall of 1893 he entered the Johns Hopkins University and after pursuing the physical-chemical course obtained the degree of Bachelor of Arts in June, 1896. Since the fall of 1896 he has been doing graduate work in Chemistry as a major subject, in Geology as a first subordinate and in Mineralogy as a second subordinate. During his residence at Hopkins he has held an ordinary Hopkins scholarship and a University scholarship. In the spring of 1899 he was appointed to a fellowship in Chemistry which he resigned in order to become Professor Remsen's assistant.

